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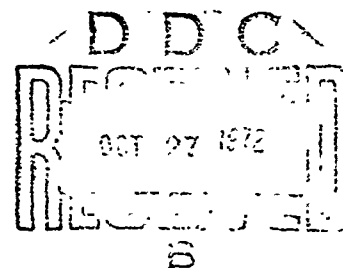
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I. INTRODUCTION

The Contract covers the period October 1, 1962 - March 31, 1972.

The research concerned various properties of semiconductors: electrical transport phenomena, optical phenomena, microwave propagation, microwave resonance, superconductivity and low-temperature thermal properties. The materials studied included elemental semiconductors and various compounds, III-V, II-VI, other compounds and oxides. The results have been reported in the semiannual progress reports throughout the years. Much of the results has also been published in various scientific journals. A summary of the work is presented in this report with emphasis on the work of recent years in the main areas. A list of the publications and a list of the PhD theses completed in connection with the research of the contract are included.

II. TECHNICAL SUMMARY

1. Galavanomagnetic Properties. W. M. Becker

Investigations have been made of the galvanomagnetic properties of III-V and II-VI semiconductors. The emphasis of the work has been the experimental investigation of the band structure and scattering mechanisms of the semiconductor.

Initial measurements in this period were carried out on a number of single-crystal samples of Te-dope n-type AlSb and undoped p-type AlSb. In n-type samples, the observed mobility behavior was explained by a combination of polar optical, acoustical mode, and ionized impurity scattering. A systematic study of the magnetoresistance gave values of the anisotropy parameter K, assuming a conduction band of silicon-like prolate ellipsoids. Magnetoresistance results on the p-type material were interpreted in terms of a model of two degenerate valence bands with warped energy surfaces, using available theoretical values of the warping parameters. The magnetoresistance behavior in both the n- and p-type samples indicated that the anisotropy decreases with decreasing temperature, a result which suggested increasing anisotropy of scattering at low temperatures due to ionized impurities.

Several studies of the effect of diffused-in lithium on the galvanomagnetic properties of n-type GaSb was investigated. In Te-doped samples, it was shown that for low concentration samples, both the carrier concentration and the mobility increase with lithium diffusion. The results suggested that the lithium ion-pairs with residual acceptor

centers. In high concentration samples, the effects are opposite, and a mechanism of formation of gallium vacancies was invoked to explain the results. A similar study carried out on Se-doped material indicated a more complicated behavior of the lithium in the GaSb lattice.

The n-type lithium-diffused GaSb samples were used in a study of the nonparabolicity of the $k = 0$ conduction band using the Shubnikov-de Haas effect as the investigative tool. The results were in good agreement with the nonparabolicity predicted by a Kane conduction-band model. Nonthermal broadening was shown to be close to the damping of the SdH oscillations expected on the basis of collision broadening.

A comparative study of deHaas-van Alphen oscillations in both the Hall effect and the magnetoresistance in Te-doped n-type GaSb was carried out at low temperatures and at high magnetic fields. The functional dependence of the Hall effect oscillations on magnetic field was shown to be similar to that of the SdH effect. Some evidence for two-band effects was seen in the monotonic behavior of the Hall effect and transverse magnetoresistance at high magnetic fields.

Following the introduction of more sensitive techniques, new details of the band structure of GaSb were revealed by Shubnikov-de Haas measurements; these showed directional beating effects, and angular anisotropy of the SdH frequency. The first effect was interpreted as evidence for inversion-asymmetry splitting of the conduction band away from $k = 0$; the second effect was shown to be consistent with warping of the Fermi surface. Similar studies were carried out on n-type HgSe. The latter investigations found that the angular anisotropy of the SdH frequency persisted to low carrier concentrations, consistent with a choice of band symmetry of Γ_8 for the conduction band of HgSe.

A short study of magnetophonon oscillations in the magnetoresistance of epitaxial n-GaAs was carried out using pulsed magnetic fields. Oscillations in both the longitudinal and transverse orientations were seen. The results were found to be inconsistent with the theory of Gurevich and Firsov.

The most recent work has emphasized the use of hydrostatic pressure and uniaxial compressional stress as additional parameters in the study of the properties of the semiconductors. Changes in the band structure of GaSb were examined using first an ice bomb pressure technique. The results obtained by this technique were verified, and then extended, using a kerosene and oil bomb technique. A model of pressure-induced carrier transfer between two conduction bands was indicated from an analysis of the data. Uniaxial stress results in the same material showed behavior suggesting carrier transfer between two conduction bands, and between minima made inequivalent by the shear components of the stress.

2. Hot-carrier Phenomena and Acoustoelectric Effects. R. Bray

The research program began with the investigation of hot carrier phenomena, primarily in p-type germanium. After some initial experiments, it became evident that it was necessary to carefully determine the strength of the various scattering mechanisms in this material. Accordingly, through studies of acoustical phonon, optical phonon, impurity and carrier-carrier scattering were carried out and reported in a series of papers terminating in 1962. This work established quantitative values for the strengths of acoustical and optical phonon scattering. These values were of critical importance in the subsequent analysis of hot carrier effects.

At first the properties of hot carriers were studied through the

changes in mobility of holes in p-type germanium with electric field strength. These results were analyzed in terms of a simple Maxwellian distribution function with a "hot carrier" temperature. When this analysis led to anomalous values for the mobility, it was suspected that the fault lay in the oversimplified treatment of the distribution function. At this stage, the first experimental measurement of the hot carrier distribution function was developed.

Use was made of the inter-valence band absorption in the infrared, involving the transitions of holes between the heavy-hole band and the split-off valence band. The hot carrier induced change in the hole population on any energy surface was measured through the resulting modulation of the infrared inter-valence band absorption. This gave energy distribution functions of hot carriers which were found to deviate quite strongly from Maxwellian distributions. Furthermore, it was possible to measure aspects of the distribution of carriers on a given energy surface in momentum space. The anisotropy of the distribution produced a birefringence which could be measured with polarized light. From these results, it was determined that the higher order terms - which are usually neglected - in the expansion of the distribution function in Legendre polynomials, were very important. From these measurements and their analysis there emerged a picture of the carriers streaming through momentum space, replacing the usual diffusion model. This effect could be attributed to the importance of optical phonon scattering in p-type germanium. The more usual diffusion picture is valid in n-type germanium, where optical phonon scattering is less important. Finally, with the empirically derived coefficients for the carrier distribution function, the mobility anomalies of hot carriers could be explained.

Following the hot carrier work, instabilities were discovered in the current under high field conditions in the III-V semiconductors. These were analyzed in detail in 1964-65 and found to involve the formation, amplification and propagation of domains of intense acoustic flux through the samples. Initial experiments were made in GaSb, and subsequently in GaAs and InSb. The effect in these semiconductors occurs primarily in the [110] direction, where piezoelectrically-active, fast-TA sound waves interact very strongly with the carriers, holes or electrons. Amplification of such phonons occurs when the carriers drift with velocity greater than the sound velocity. The acoustoelectric gain can greatly exceed lattice attenuation over a wide frequency range, and permits build-up of acoustic flux to very intense proportions, affecting both the electrical and optical properties of the materials. The evolution of the domains of acoustic flux was followed initially by electrical probe measurements of the associated high electrical fields in the domain. Later an optical probe technique was developed based on the discovery of the broadening of the intrinsic absorption edge by the intense acoustic flux. The most fruitful technique was that of Brillouin scattering. Such studies yielded the spectral and angular composition of the amplified phonons, as well as their spatial distribution. It was possible to follow the evolution of acoustic flux through a linear gain region, into a non-linear regime where parametric frequency conversion processes dominated. The acoustic flux ultimately grows to some 10^{10} times above the thermal equilibrium value, making the detection of the intense flux by Brillouin scattering exceedingly simple. The intense growth is restricted to the piezoelectric phonons in a broad frequency range determined by the electrical properties of a given sample, and to a cone of about 10° about the [110] direction.

Another interesting discovery was the strong control of the acousto-electric effect by transverse and longitudinal magnetic fields. The former can be understood in terms of simple theory, but not the latter. Extensive studies were made of the effects of magnetic field on phonon amplification, domain formation, and the form of the instabilities in p- and n-type InSb and in bulk and epitaxial GaAs. New anomalies were discovered in strong magnetic field and strong acoustic flux, both for transverse and longitudinal magnetic fields.

Most recently the amplified acoustic flux was used as a very convenient source of phonons to study basic properties, such as acoustic gain and lattice attenuation, and also their dependence on magnetic field, over a very wide frequency range, 0.30-5.0 GHz, at room temperature. In addition, it has been possible by several techniques to convert the amplified fast-TA phonons into non-piezoelectrically-active slow-TA phonons and LA phonons, thereby providing additional opportunities for such basic studies. A most interesting application is the use of the intense phonon beams to study resonant Brillouin Scattering near the absorption edge, the intense beam permitting detailed dispersion measurements with relatively weak, but spectrometer-tuned light sources. Finally, a study of the modulation of the intrinsic absorption edge by the intense flux was undertaken in terms of a comparison of the effects of fast-TA, slow TA and LA phonons. Only the former modified the absorption edge, from which it could be deduced that the microscopic longitudinal piezoelectric fields of the fast-TA phonons were predominantly responsible for the effect through a Franz-Keldysh type mechanism. This bears important relevance for current

theories of the Urbach effect, involving natural broadening of the absorption edge.

3. Electrical and Ultrasonic Transport Phenomena, R. J. Sladek

a) Effect of Stress on Electrical Transport

Impurity levels in n-type GaAs. We discovered that the electrical properties of n-GaAs having room temperature carrier concentrations between 10^{14} and 10^{16} were stress dependent at quite low stress levels. Studies made to determine why revealed that changes in the degree of ionization of non-shallow donors were responsible. The ionization energy of these donors was about .17eV and increased with increasing stress at a rate similar to that at which the $\langle 100 \rangle$ subsidiary conduction band minimum moved down relative to the $k = 0$ minimum. Comparison of the concentration of non-shallow donors deduced from the electrical measurements with the results of mass spectroscopic analyses suggested that carbon, nitrogen, or oxygen were possible sources of the .17eV donor levels.

Sulfur levels in silicon. The Hall effect and resistivity of Si doped with S were measured as a function of temperature between 300K and 50K and as a function of hydrostatic pressure up to 8 kbar at various temperatures. From the Hall effect data the ionization energies and their temperature and pressure dependences were obtained for the A, B, and C sulfur levels. The further the level lay below the conduction band, the larger was the shift toward the conduction band caused by a given amount of pressure. A group theoretical analysis of which Bloch waves can appear in localized impurity wave functions of various symmetries was used to deduce information about the symmetry of an impurity center from the pressure shift of its ionization energy. Thus, the D center (observed by others) is a

substitutional S^+ at a T_d site; the C center is an S_2^+ -center with D_{3d} symmetry; the B center is a neutral version of the C center; and the A center may represent the effects of interstitial sulfur at D_{3d} sites. The Hall mobility at zero applied pressure indicated that scattering by lattice vibrations, ionized impurities, neutral impurities and agglomerations of sulfur were all important. The dependence of the mobility on pressure was due, partly to a decrease of effective mass with increasing pressure.

Band structure and deformation potential in AlSb. Piezoresistance and piezo-Hall effect measurements employing hydrostatic pressure and uniaxial stress were made on n-type and p-type AlSb. Results on n-type material established that the conduction band is multivalleyed with valleys along $\langle 100 \rangle$ axes in k space with a shear deformation potential constant $\Xi_u = 6.2 \pm 0.4$ eV at room temperature. p-type AlSb exhibited piezoresistance behavior which was consistent with a degenerate valence band edge similar to that in other III-V semiconductors.

b) Impurity Conduction in Magnetic Fields

n-Ge. A study of impurity conduction mechanisms in n-type Ge doped with small and intermediate concentrations of phosphorus was made by means of magnetoresistance measurements at liquid helium temperatures. Some of the results were similar to those obtained previously by Sladek & Keyes on Ge doped with small amounts of Sb or As so as to be in the phonon-assisted, hop conduction range and could be explained in terms of the effect of the magnetic field on the size and shape of the wave function of the outermost electron on the P donor. However, it was discovered that the magnitude of the magnetoresistance exhibited a direct dependence

on donor concentration at the higher P concentrations where " ϵ_2 -type" impurity conduction was expected to predominate. Current theories could not account for this concentration dependence of the magnetoresistance. The anisotropy of the magnetoresistance was found to be similar in all samples implying that some conduction may be due to hopping of electrons between donors in samples where non-hopping processes are thought to predominate.

p-Ge. The magnetoresistance of hop conduction in p-type Ge was measured in fields up to 25 kG for the first time. The results were generally explainable in terms of the influence of the magnetic field on the acceptor wave functions although no specific formula for the anisotropy of the magneto-resistance was available for comparison with the data. A semiquantitative interpretation of some of our results was made by employing theory developed by others for a semiconductor with a simple, spherical band at $k = 0$ which included the influence of the magnetic field on the relative phase of the wave functions on adjacent acceptors as well on the extent of the wave function on a given acceptor.

Epitaxial n-GaAs. Measurements of the Hall effect and resistivity of epitaxial n-GaAs were made at liquid helium temperatures in fields up to 26 kG. They revealed that the Hall coefficient exhibited strong increases or decreases with magnetic field strength depending on the temperature. Analysis of our data indicated that magnetic freezeout took place and that donor impurity states are modified by the magnetic field in such a way that the Hall effect of carriers in these states decreased as the magnetic field increased.

C) Ultrasonic Studies

Ultrasonic attenuation in InAs at low temperatures. The attenuation of

ultrasonic waves propagating in the [110] direction in InAs was measured between 1.5K and 100K at frequencies between 150 MHz and 510 MHz. Analysis of the results indicated that the temperature dependent part of the attenuation was due to three-phonon collision processes between the low energy phonons of the longitudinal, or the slow shear, sound wave and transverse thermal phonons. Values for certain averages involving the third order elastic constants were deduced.

Relaxation attenuation in InAs. The attenuation of longitudinal and transverse ultrasonic waves with frequencies between 90 MHz and 510 MHz propagating in the [110] direction in InAs was measured at room temperature. When the residual attenuation observed at 4.2 K was subtracted from the measured attenuation, the remaining attenuation approached a quadratic frequency dependence as expected for the Akhieser phonon-viscosity mechanism. The attenuation of 210 MHz longitudinal waves was also measured at lower temperatures. It was found that temperature dependence could be accounted for by the Akhieser mechanism and was due mainly to the quantity $\sum_i \gamma_i^2 C_{v_i}$ where the γ_i 's and C_{v_i} 's are the Gruneisen γ 's and heat capacities, respectively, of a small number of Debye continua and Einstein modes by which the actual phonon spectrum can be approximated. Our result indicated that a large part of the temperature dependence of phonon viscosity attenuation could be understood by a more realistic treatment of the heat capacity and Gruneisen parameter.

Velocity and attenuation of ultrasonic waves in III-V. Compound Semiconductors at Low Temperatures. Measurement of the velocity and attenuation of ultrasonic waves in n-type GaAs, undoped or doped with oxygen, has revealed anomalies in the temperature dependence of these quantities for [110] [001] shear waves below about 160K. The anomalies are correlated with the

freezing out of electrons from the conduction band into non-shallow impurity levels as the temperature decreases. The freeze-out of electrons is accompanied by a vanishing of the screening of the piezoelectric interaction between lattice ions and an enhancement in the velocity of the [110] [001] shear modes. A large maximum in the attenuation occurs at temperatures in the vicinity of the velocity enhancement. Both the velocity enhancement and the size of the attenuation peak yield a value for the piezoelectric constant $e_{14} = 0.16 \text{ C/m}^2$.

Attenuation of ultrasound in amorphous As_2S_3 . Investigation of the frequency dependence of the ultrasonic attenuation in glassy As_2S_3 was begun in order to look for structural and relaxation effects. Initial results indicated a different type of frequency dependence than that observed in crystalline insulators. However, more accurate data is needed before an interpretation is attempted.

4. Optical Properties. H. Y. Fan

a) Optical and Electrical Properties of ZnSb

Single crystals of p-type ZnSb have been grown by pulling from the melt. The carrier concentration is of the order of 10^{16} cm^{-3} . The Hall mobility is of the order of a few hundred $\text{cm}^2/\text{sec-V}$ at room temperature, and is highest for current along the c axis and lowest for current along the b axis. Indirect and direct transitions have been observed in the absorption edge. The indirect transitions begin at the photon energy: 0.50 eV at 300°K , 0.59 eV at 77°K , and 0.61 eV at 4.2°K , independent of polarization. The direct transitions appear to begin at the lowest photon energy for $E \parallel c$ and at the highest photon energy for $E \parallel a$. The carrier absorption at long wavelengths is highest for $E \parallel c$. The results

indicate that the valence band has three closely spaced bands near the maximum which corresponds to either the point Γ or the points R of the Brillouin zone, while the minimum of the conduction band is at the other position. The effective mass tensor of holes is estimated.

b) Impurity and Exciton Effects on the Absorption Edge of III-V Compounds

The fundamental absorption edge of each of several III-V compounds has been examined for structure due to excitons and impurities using high resolution and sample temperatures down to 1.4°K . The effects of an applied magnetic field were studied. The absorption edge of GaSb shows three sharp peaks (α , β , γ) and a low-absorption tail. Under a magnetic field, the peaks (α , β , γ) shift and split in a manner close to the expected behavior of the exciton. The peak α is shown to be the free-exciton peak and the peaks (β and γ) are attributed to impurity-exciton complexes. The tail is found to be associated with electron transitions to the conduction band from impurity levels near the valence band. Absorption associated with impurity-valence-band transitions is also observed at low photon energies. Analysis of these results gives the energy gap, the electron g factor, and the ionization energies of impurity levels. The absorption edge of InSb shows a step which is found to be due to ionized acceptors. Under a magnetic field, two peaks develop from the step absorption which behave like the impurity-exciton peaks in GaSb. The optical transitions involved appear to be related to the emission observed in the InSb laser. The electron g factor and the ionization energies of impurity levels have been estimated from these results. Some studies on the impurity absorption near the intrinsic edge of other III-V compounds are reported.

c) Optical Properties of ZnTe.

The optical absorption of ZnTe single crystals grown by the Bridgeman

method has been studied from visible wavelengths to $50\ \mu$, at temperatures from 1.4 to 300°K . Lattice combination bands are observed from which assignments of zone-boundary phonon energies are made. Absorption due to inter-valence-band transitions indicates the presence of two bands degenerate at $k = 0$ and a split-off band lying 1 eV below. Infrared absorption is observed for As impurity and for a residual impurity in undoped material, probably a zinc vacancy. For each impurity, absorption due to transitions to the split-off valence band is also observed near 1 eV. Sharp excitation lines are seen in the spectrum of the residual impurity. The lines are repeated with emission of optical phonons of energy 0.026 eV, from which the electron-phonon coupling coefficient is estimated. Some structure is observed also in the spectrum of As impurity. A tail is observed at the absorption edge which shows the effect of various impurity levels in the undoped material and in the samples doped with As, In, or Fe. In two samples grown from the vapor phase, some sharp absorption lines are present in the range 2.2 to 2.35 eV. These lines are apparently due to exciton-impurity complexes. Photoconductivity and reflection have been measured. The spectrum of photoconductivity shows oscillations. From the results, the intrinsic energy gap and the effective masses of electrons and holes are determined.

d) Faraday Rotation in p-Type Semiconductors.

Faraday rotation has been investigated for p-type germanium, gallium arsenide, gallium antimonide, indium arsenide, and zinc telluride from the neighborhood of intrinsic absorption edge up to $20\ \mu$. The spectra show maxima and minima resulting from electron transitions between various sets of Landau levels which are associated with the two degenerate hole bands and the spin-orbit band. Transitions between levels in the same sets

correspond to the free-carrier effect of a simple energy band, giving a rotation proportional to λ^2 . Transitions between the levels of the spin-orbit band and those of the two hole bands produce a structure in the rotation spectrum which is observed in the case of Ge and GaAs, where the spin-orbit splitting is smaller than the energy gap. At long wavelengths, transitions between levels associated with different hole bands are important. In ZnTe, a different spectrum is observed at low temperature, which is produced by holes bound to impurities. The dependence of Faraday rotation on carrier relaxation time has been studied for germanium. The magnitude of rotation is found to decrease with decreasing relaxation time. Theoretical calculations are made for germanium. Satisfactory agreement with the experimental data is obtained.

e) Phonon-cyclotron Resonance and Carrier-Transfer resonance in the Infrared Absorption.

A series of peaks has been observed in the infrared absorption by free carriers in n-type InSb under applied magnetic field. With decreasing field, the peaks converge to an energy equal to that of a LO phonon. The energy separations between the peaks are related to the separations of Landau levels. These peaks are called phonon cyclotron resonances, and they are associated with indirect transitions involving LO phonons. A theory is presented which accounts for various aspects of the observation including the positions and the strengths of the resonances as well as the effect of polarization on the resonances. Some peaks were observed in addition to the phonon cyclotron resonances, which appear to represent the third harmonic of cyclotron resonance and the second harmonic with spin flip.

Phonon-cyclotron resonance has been studied also in n-InAs and in the many-valley semiconductor n-PbTe. In PbTe, the effects of magnetic field orientation relative to the crystallographic axes of the crystal and special effects of polarization of radiation has been observed, and the anisotropic effective mass of the electron are determined. A new type of resonance absorption, carrier-transfer resonance, which is characteristic of a many-valley band has been discovered.

f) Raman Scattering and Optical Absorption in KTN.

Raman scattering from the mixed crystal $\text{KTa}_{0.64}\text{Nb}_{0.36}\text{O}_3$ ($T_c \approx 10^\circ\text{C}$) has been investigated as a function of temperature in the paraelectric and single-domain-ferroelectric phases. The phonon spectrum was found to correspond predominantly to that of the host lattice of KTaO_3 . Significant effects due to the mixed nature of the crystal were found. In the ferroelectric phase, first-order lines were observed with symmetry properties forbidden for an ideal perovskite structure. Also, two Raman lines in the ferroelectric phase are attributed to local modes associated with the Nb ions in the lattice. In the paraelectric phase, lines observed at 202 and 279 cm^{-1} persisted as first-order structures. The behavior of the 279-cm^{-1} line was found to be consistent with a reduction of the phonon symmetry from F_{2u} to F_2 , which could be caused by a relaxation of the inversion symmetry of the cubic lattice. The persistence of the 202-cm^{-1} line cannot be accounted for by the loss of inversion symmetry and may be due to the relaxation of translational symmetry. First-order structures occurred also at 175 and 436 cm^{-1} , and are attributed to zone-boundary phonons. First-order scattering was induced in the paraelectric phase by the application of an electric field to the sample. For comparable values of

polarization, the intensity of the induced first-order scattering measured just above the transition temperature was found to be substantially less than the intensity of the spontaneous first-order scattering measured just below the transition temperature. Existing theory predicts that the spontaneous and induced scattering intensities should be nearly equal for these conditions.

The splitting of the conduction-band edge, deduced from the dichroism of the absorption edge, has been studied for insulating $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ ($T_c \approx 5^\circ\text{C}$) as a function of applied electric field and temperature in the paraelectric and single-domain ferroelectric phases. In the paraelectric phase, the polarization-dependent splitting can be represented by the expression $\Delta\mathcal{E} = aP^2 + bP^4$. The coefficients a and b are substantially the same in both the paraelectric and ferroelectric phases. The fourth-order term is attributed to higher-order effects of the change in the Ta (Nb) - O spacing on the band edge. The observed deviation from a purely quadratic polarization dependence appears, within the experimental uncertainty, to be independent of temperature and, thus, does not support a polarization-fluctuation model recently proposed to explain a similar deviation observed in ferroelectric BaTiO_3 .

5. Microwave Propagation in Semiconductors. J. K. Furdyna

Much of the early work was involved with the interpretation of previously obtained data on microwave helicon propagation in bulk semiconductors. Helicon dispersion and damping were examined theoretically, and compared with the data from experiments on such materials as Ge, InAs, and InSb. Both intrinsic and extrinsic materials were studied from 4.2°K to room temperature in magnetic fields up to 150 kG. Quantum, spin, and high field damping effects, and

quantum oscillations in the helicon dispersion were also reported. Some preliminary data on magnetoplasma wave propagation in pyrolytic graphite, and in powdered semiconductors and semimetals, were also analyzed.

More recently, the graphite and powder studies have been extended. Alfven wave propagation and damping were investigated in single crystal as well as pyrolytic graphite. Also, both local and non-local effects were examined. Microwave experiments through semiconductor powders studied helicon-like waves, dimensional resonances, and magnetoplasma resonances. Powder samples of InSb, InAs, HgTe, and HgSe with a relatively large carrier concentration were used for this investigation. Also, microwave excitation of single particles was studied. The main features of the powder and single particle experiments were explained in an extensive theoretical study.

At present, the emphasis is on microwave helicon experiments in semiconductors doped with magnetic impurities. The interest in these experiments lies in the possible coupling between helicons and the magnetic impurities.

6. Microwave Electron-Spin-Resonance in Semiconductors. R. L. Mieher

A considerable advance in our experimental and theoretical understanding of the ground state of the shallow donor electron has been achieved. In fact, the shallow donor electron is now probably the best understood bound state electron in solid state physics. The measurements

of the experimental electron-nuclear double resonance (ENDOR) hyperfine tensors for the Si^{29} lattice nuclei near the shallow donor impurities As, P, and Sb have been extended from the original measurements (by Prof. G. Feher) of 5 independent lattice sites to 25 independent lattice sites. Since the hyperfine tensor consists of 2, 3, or 4 independent

numbers, our measurements result in about 175 independent numbers that characterize the problem in considerable detail.

The interpretation of the experimental data has required an extensive theoretical effort. The first theory of the anisotropic hyperfine interaction was developed using the effective mass theory (EMT) wavefunction and an equivalent orbital representation of the conduction band minima Bloch functions. This theory provided the first qualitative and semiquantitative explanation of the experimental values.

Since the effective mass theory wavefunction was not accurate enough to interpret most of the experimental data, a major effort was made to obtain a more accurate wavefunction. The new wavefunction was represented as an expansion in reciprocal lattice space in terms of Bloch function throughout the Brillouin zone for several energy bands. This work was successful and permitted interpretation of the experimental data for the first time.

The new wavefunction was obtained in terms of pseudopotential Bloch functions which were accurate enough for calculating the Fermi contact part of the hyperfine tensor since it depends on the s part of the Bloch functions.

On the other hand the anisotropic part of the hyperfine tensor depends on the p and d character of the Bloch function. It was determined that the pseudopotential Bloch functions do not have sufficient d character to explain the experimental results. Therefore, a very exact LCAO representation of the Bloch functions has been developed. The LCAO representation has made it possible to explain the anisotropic part of the hyperfine tensors. We believe that the theoretical techniques that we have used will be applicable to other semiconductor problems.

7. Superconductivity and Specific Heat. P. H. Keesom

In 1957 Bardeen, Cooper and Schrieffer published a theory to explain superconductivity. They calculated that the electronic contributions to the specific heat is exponential and could be written:

$$C_{es} = \gamma T_c \cdot a \cdot e^{-bT_c/T}.$$

In this formula γT_c is the electronic specific heat in the normal state at the transition temperature T_c ; a and b are constants and were calculated in this theory. Immediately after this theory was published we started to investigate the specific heat of many elemental superconductors, partially to compare with the theory, partially to provide data on the lattice specific heat and in addition, through several thermodynamic formula, the critical field H_c as a function of T .

In 1961 Bryant and Keesom published results on indium, which still are not understood. On theoretical grounds it is expected that the lattice contribution to the specific heat does not change when the metal transforms from the normal to the superconductive state. As a consequence the lower limit of the specific heat in the superconductive state should be the lattice contribution when the electronic part has died out exponentially. This is not the case for indium, as for this element the lowest specific heat in the superconductive state is well below that what was found for the lattice specific heat in the normal state. In the beginning of this period we investigated several other elements which have high transition temperatures, like thallium, mercury and lead. Useful data were obtained, but the anomaly for indium did not show up. After the results for indium were published another group of investigators claimed that niobium showed the same anomaly. However we were able to show that their investigations did not

extend to sufficiently low temperatures.

In 1966 Radebaugh and Keesom published their results on the element vanadium. They were able to show that this is the second type II superconductor and investigated in considerable detail the mixed state, in which this element is superconductive, but allow magnetic field to penetrate, as distinct from the type I superconductors, which exclude completely any magnetic flux in the superconductive state. The whole thermodynamic diagram for vanadium was investigated and compared with the many theories, especially with the work of Maki.

As a sideline of the investigation the specific heat of graphite was investigated. At the starting time of this investigation it was known, from previous work supported by the Army contract, that the specific heat of graphite differs for different samples. One theory explained this by the assumption that the structure of graphite shows stacking faults, that is successive layers of graphite are somewhat randomly arranged and contribute to the specific heat. However a second theory thought that the difference in specific heat was a consequence of surface modes of the graphite crystallites. Specific heat results of pyrographite was decisive in favor of the stacking fault theory. In this pyrographite the crystallites are very large so that there are relatively few surface modes, but the randomness between the layers is very large. A large increase in the specific heat was observed, which showed that the stacking faults contribute to the specific heat.

A completely different research has been carried out on the oxides of titanium: TiO_2 (rutile) pure and reduced, and Ti_2O_3 , pure and doped with vanadium. Reduction makes rutile conductive and vanadium doping makes Ti_2O_3 metallic. These metallic compounds show increases in the specific heat as

compared to the pure material of many orders of magnitude at very low temperatures. The increase in specific heat is probably of electronic origin. A detailed discussion on the bandstructure implication for rutile was published. For Ti_2O_3 the results are even more interesting. The excess specific heat can be explained by the assumption that the band structure is similar to that of an one-dimensional electron gas. This explains why the very lowest part of the excess specific heat is inversely proportional to the amount of added vanadium. And also why the specific heat becomes constant at higher temperatures, a feature of a classical electron gas. Numerical calculations for 5 different samples, using this model shows an excellent agreement. This work is being pursued.

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